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Double thermal donors in Czochralski-grown silicon heat-treated under atmospheric and high hydrostatic pressures

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The formation kinetics of Thermal Double Donors, a dominant family of thermal donors in Czochralski-grown silicon annealed at $T < 600$ °C, is studied in detail. A striking enhancement effect of hydrostatic pressures of about 1 GPa on their formation processes, even in a temperature region of thermal instability of these donor centers at about $T = 600$ °C under normal conditions, is clearly demonstrated. The experimental data obtained in the present work are in agreement with the recent theoretical calculations of oxygen diffusion and agglomeration processes in heat-treated Si.

It is well known that oxygen impurity atoms in Czochralski-grown silicon (Cz–Si) being available in concentrations much higher than the oxygen solubility at room temperature are prone to agglomeration upon heating. Heat treatment of Cz–Si at $T < 500$ °C gives rise to the formation of a family of Thermal Double Donors (TDDs) consisting of more than 16 centres with shallow and deep energy states in the regions between 44 meV and 70 meV and between 100 meV and 150 meV, respectively [1, 2]. The electrical properties of Cz–Si heat treated at $T < 500$ °C are mainly determined by this family of thermal donors. The characteristic features of oxygen diffusion and agglomeration processes in annealed Cz–Si have recently been reviewed in [3]. Despite a vast amount of information available in the literature the key steps in these processes are still a matter of discussion. Among many well-known factors producing considerable effects on the TDD formation processes, e.g. heat-treatment regimes, the presence of isovalent impurities C and Ge, and so on, the effects of compressive stresses of about 1 GPa leading to enhanced formation of thermal donors in annealed Cz–Si [4, 5] are relatively little studied. The purpose of the present work is to study the formation kinetics of TDDs in a more systematic way. This provides a solid basis for computational simulations giving a clue for the complex nature of oxygen aggregates in Si.

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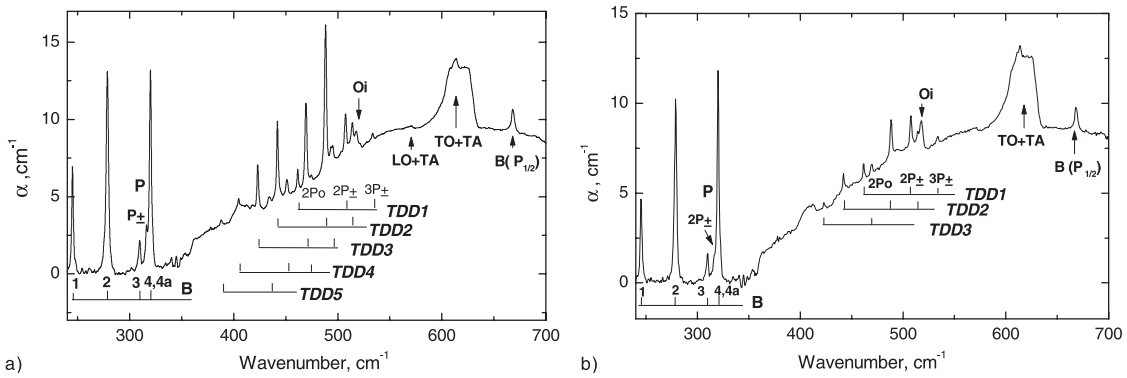

Fig. 1 IR absorption spectra for the Cz–Si heat treated at T = 450 °C (a) and 600 °C (b) for t = 2 h (a) and 10 h (b), under a hydrostatic pressure of P = 1.2 GPa. Initial oxygen concentration, $N^0_{oxy} = 6.0 \times 10^{17}$ cm^{-3}. Before measurements the sample was cooled down to T < 6 K under bandgap illumination. The spectrum was also recorded under bandgap illumination. The known 2p-transitions of the neutral TDD species are given. Some identified transitions of the shallow centers of P and B are also shown.

Several wafers of carbon-lean Cz–Si, undoped and doped with B and P, were used. The initial oxygen concentrations in samples were below or higher than a critical value of about 7×10^{17} cm^{-3}, as determined by the oxygen absorption band at 1108 cm^{-1} using a conversion factor of 2.45×10^{17} cm^{-2}. Oxygen precipitation processes are well known to be rather sensitive to the initial oxygen content with respect to the critical one, especially at T > 500 °C. Two classical regimes of heat treatment were used for a comparative study, at T = 450 °C and 600 °C, respectively, both at atmospheric pressure in nitrogen and hydrostatic pressures of about 1 GPa in pure argon. A temperature region around T = 450 °C is known to be appropriate for the most effective production of TDDs, whereas that around T = 600 °C is a region of thermal instability of TDDs. IR absorption and photoconductivity spectra at T < 6 K were recorded using a IFS-113V Bruker spectrometer. The resolution was 1 cm^{-1}. Hall effect measurements over a temperature range of T = 20 K to 300 K were taken by means of the Van der Pauw technique. Electrical data were analyzed with the help of the relevant equations of charge balance.

For illustration purposes, in Fig. 1 and Fig. 2 some optical and electrical data are given. Hall effect data allow one to estimate the total concentrations and effective ionisation energies of shallow and deep centres. Optical spectra permit one to identify each species of the TDD family and estimate its absolute concentration using the optical cross sections of the $2p_0$-transitions of the neutral TDDs [6].

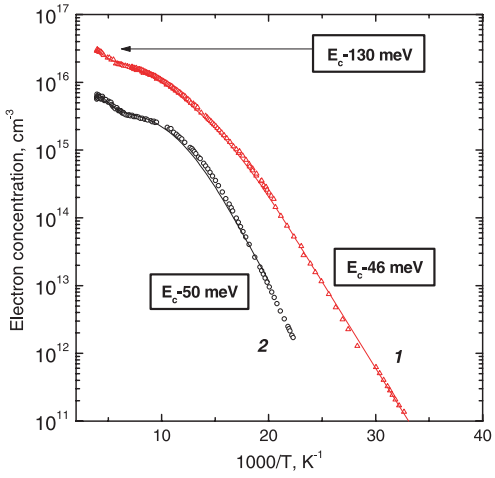

Fig. 2 (online colour) Electron concentration *versus* reciprocal temperature in the Cz-Si heat treated at T = 450 °C for t = 10 h under a hydrostatic pressure of P = 1.2 GPa. Initial oxygen concentrations N^0_{oxy} (in cm^{-3}): 1) 9.5×10^{17}; 2) 6.0×10^{17}. The effective activation energies of thermal donors are given. Both initial materials were p-type, with boron concentrations in the low 10^{15} cm^{-3}.

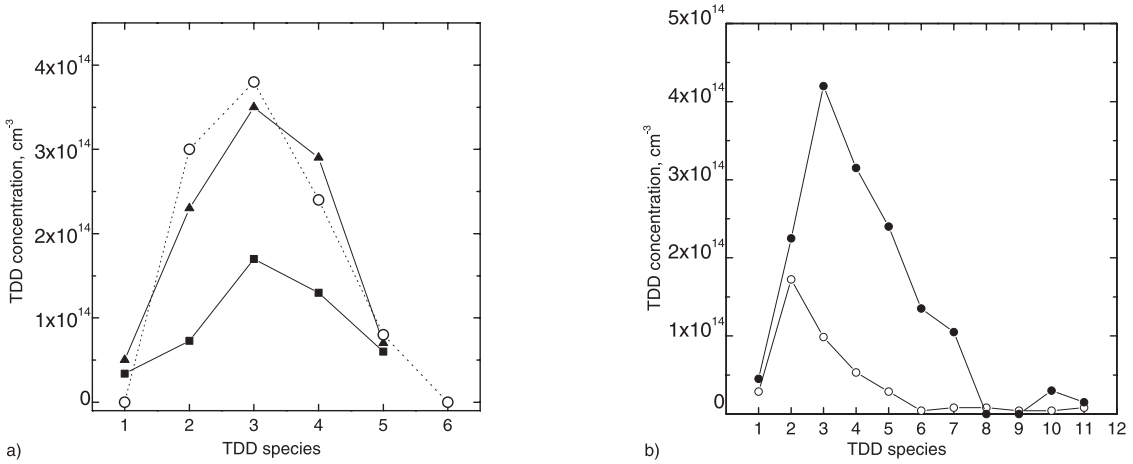

Fig. 3 TDD distributions in the heat-treated Cz–Si with initial oxygen concentrations of $N^0_{oxy} = 6.0 \times 10^{17}$cm^{-3} (a) and 8.0×10^{17} cm^{-3} (b). a) Heat treatment at $T = 450$ °C for $t = 30$ h (solid squares) and 60 h (solid triangles) at atmospheric pressure. For comparison, the TDD distribution in the same Cz–Si heat-treated at $T = 450$ °C for $t = 10$ h under a hydrostatic pressure of $P = 1.0$ GPa is also shown (open circles). b) Heat treatment at $T = 450$ °C for $t = 4$ h (open circles) and 16 h (solid circles) at atmospheric pressure.

In Fig. 3 the formation kinetics of TDDs under normal conditions is shown for the Cz–Si samples with different oxygen contents. It is clearly seen that at low oxygen contents the maximum of the TDD distributions is placed at the same position up to $t = 60$ h (Fig. 3a), whereas at high oxygen contents it starts to move to the higher-numbered species just at the beginning of heat treatment (Fig. 3b). At present many features of the TDD formation kinetics shown in Fig. 3 can be satisfactorily described in the framework of a general kinetic model with parameters based on accurate *ab initio* total-energy calculations [7]. This kinetic model of oxygen agglomeration in heat-treated Cz–Si includes all relevant association, dissociation and rearrangement processes.

As is seen from Fig. 3a, a striking enhancement of the TDD formation is observed in stressed Cz–Si; cf two curves for $t = 60$ h under normal conditions and 10 h under a hydrostatic pressure of 1.0 GPa. The formation kinetics of TDDs in stressed Cz–Si with different oxygen contents is shown in Fig. 4. The peculiarities of both TDD distributions, as compared to those produced at atmospheric pressure, are well

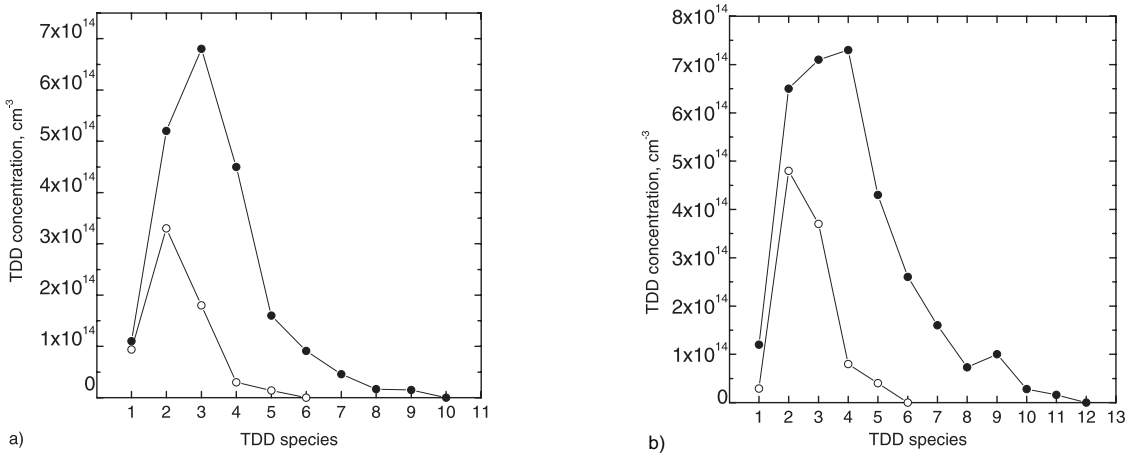

Fig. 4 TDD distributions in the heat-treated Cz-Si with initial oxygen concentrations of $N^0_{oxy} = 6.0 \times 10^{17}$ cm^{-3} (a) and 9.5×10^{17} cm^{-3} (b). Heat treatment at $T = 450$ °C for $t = 2$ h (open circles) and 10 h (solid circles) under a hydrostatic pressure of $P = 1.2$ GPa.

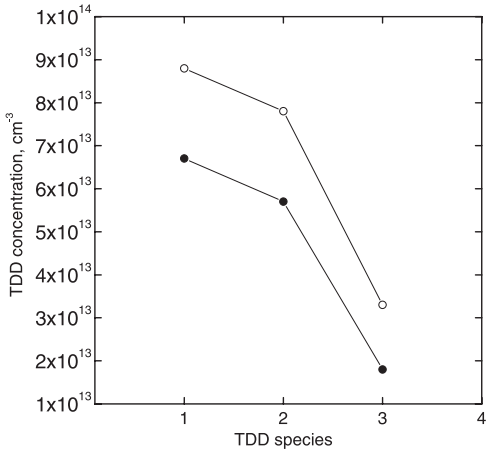

Fig. 5 TDD distributions in the heat-treated Cz–Si with initial oxygen concentrations of $N^0_{oxy} = 6.0 \times 10^{17}\,cm^{-3}$ (solid circles) and $9.5 \times 10^{17}\,cm^{-3}$ (open circles). Heat treatment at $T = 600$ °C for $t = 10$ h under a hydrostatic pressure of $P = 1.2$ GPa.

pronounced, especially at the maximum; cf Fig. 3 and Fig. 4. The enhanced formation of TDDs under compressive stress is thought to be due to increasing oxygen diffusivity. It has been calculated that the local vibrational modes of isolated oxygen atoms and staggered oxygen dimers, both units playing an important part in the diffusion processes, are changed with hydrostatic pressures at about 1 GPa [8].

At temperatures of heat treatment $T > 600$ °C under normal conditions the TDD formation in Cz–Si is known to be of insignificant importance, if at all. In actual fact, the presence of TDDs in Cz–Si heat treated at $T = 600$ °C for $t = 24$ h can be barely detected in photoconductivity spectra. Their total concentration was found to be about 1×10^{13} cm^{-3}. Application of compressive stress to Cz–Si during heat treatment gives rise to an enhanced formation of TDDs, so they are getting visible in IR absorption spectra; see Fig. 1b. In this case their total concentration runs up to 2×10^{14} cm^{-3} for $t = 10$ h. The TDD distributions given in Fig. 5 show a dominant formation of only the low-numbered species.

In conclusion, detailed information on the formation processes of Thermal Double Donors in Cz–Si heat treated at $T = 450$ °C and 600 °C at atmospheric pressure and compressive stress is obtained. Enhancement effects of high hydrostatic pressure on these processes are very much pronounced, even at $T = 600$ °C. The data form a solid basis for computational analysis of the oxygen diffusion and agglomeration processes in Czochralski-grown silicon upon annealing. Some preliminary results of such calculations are promising.

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